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(54) SURFACES STRUCTUREES HYDROPHOBES
(54) STRUCTURED SURFACES HAVING HYDROPHOBIC PROPERTIES

(57)

Disclosed is an article having a structured surface, wherein the structured surface has protuberances having an average height of 50 nm to 10 ~m and an average spacing of 50 nm to 10 ~m and the structured surface is made of a material which is hydrophobic to such an extent that the material has, when unstructured, a surface energy of 10 to 20 mN/m. The surface has a large contact angle with water, is hardly wetted by water and therefore has a self-cleaning effect. Also disclosed are processes for the production of the article.

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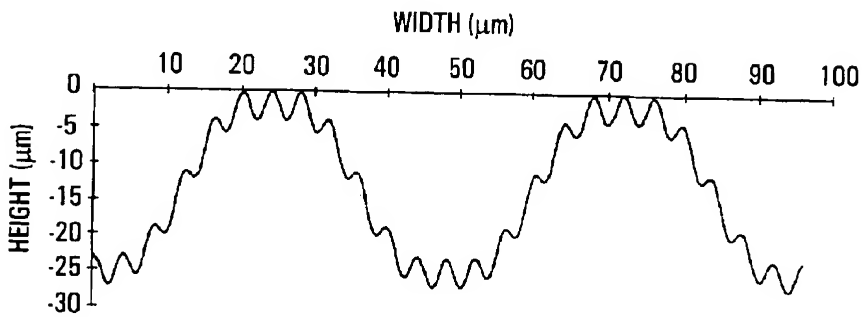
(54) **SURFACES STRUCTUREES HYDROPHOBES**
(54) **STRUCTURED SURFACES HAVING HYDROPHOBIC PROPERTIES**



(57) Disclosed is an article having a structured surface, wherein the structured surface has protuberances having an average height of 50 nm to 10 .mu.m and an average spacing of 50 nm to 10 .mu.m and the structured surface is made of a material which is hydrophobic to such an extent that the material has, when unstructured, a surface energy of 10 to 20 mN/m. The surface has a large contact angle with water, is hardly wetted by water and therefore has a self-cleaning effect. Also disclosed are processes for the production of the article.

Abstract

Disclosed is an article having a structured surface, wherein the structured surface has protuberances having an average height of 50 nm to 10 μm and an average spacing of 50 nm to 10 μm and the structured surface is made of a material which is hydrophobic to such an extent that the material has, when unstructured, a surface energy of 10 to 20 mN/m. The surface has a large contact angle with water, is hardly wetted by water and therefore has a self-cleaning effect. Also disclosed are processes for the production of the article.

STRUCTURED SURFACES HAVING HYDROPHOBIC PROPERTIES

Field of the Invention

The present invention relates to articles having structured surfaces made of materials having low surface energy.

The present invention furthermore relates to processes for the production of these articles having structured surfaces.

Background of the Invention

Articles having surfaces which are difficult to wet have a number of interesting and economically important features. For example, they are easy to clean and do not easily retain residues. These properties relate in particular to transparent and aesthetically appealing articles.

Surfaces from which water readily runs off must be either very hydrophilic or hydrophobic. Hydrophilic surfaces have a small contact angle with water, resulting in rapid distribution of the water over the surface and finally rapid running off of the resulting water film from the surface.

Hydrophobic surfaces, on the other hand, ensure drop formation by means of a large contact angle with water. These drops can rapidly roll off inclined surfaces.

The use of hydrophobic material, such as perfluorinated polymers, for the production of hydrophobic surfaces is known; a further development of these surfaces consists in structuring the surface in the μm to nm range.

U.S. Patent No. 5,599,489 discloses a process in

which a surface can be rendered particularly water-repellent by bombardment with particles of an appropriate and subsequent perfluorination.

Another process is described by H. Saito et al. in Surface Coating International 4, 1997, page 168 et seq. Here, particles of fluorine polymers were applied to metal surfaces resulting in greatly reduced wettability of the surfaces with respect to water. A considerably reduced tendency to icing was also found.

U.S. Patent No. 3,354,022 and WO 96/04123 described further processes for reducing the wettability of articles by topological changes to the surfaces. Described therein are artificial protuberances or indentations, having a height of about 5 to 1000 μm and a spacing of about 5 to 500 μm, which were applied to hydrophobic materials, or materials rendered hydrophobic after the structuring. Surfaces of this type lead to rapid drop formation, the drops which roll off picking up dirt particles and thus cleaning the surface. No information is given regarding an aspect ratio of the protuberances.

Surfaces of this type have a large contact angle with water but are completely wetted by liquids such as oil. Once wet, the effect of the large contact angle with water, which results from the structure, is also lost. The use of such material is thus limited to areas where no liquids forming an oil film occur.

It is therefore a major object of the present invention to develop industrially useful surfaces which have a

very large contact angle with water and from which dirt, in particular oily dirt, can be removed, for example, by washing off with water, or which promote the running off of water.

It was surprisingly found that structured surfaces having protuberances with a height of 50 nm to 10 μm and an average spacing of 50 nm to 10 μm and a surface energy of the unstructured material of 10 to 20 mN/m are virtually not wetted by water and can also be readily cleaned to remove oily dirt.

Summary of the Invention

The present invention therefore relates to an article having a structured surface, wherein the structured surface has protuberances having an average height of 50 nm to 10 μm and an average spacing of 50 nm to 10 μm and the structured surface is made of a material which is hydrophobic to such an extent that the material has, when structured, a surface energy of 10 to 20 mN/m.

The present invention furthermore relates to a process for the production of the article wherein protuberances are formed by mechanical impression or are etched by lithographic methods or are applied by shaping.

Materials for the purposes of the present invention are products which already have their final form for use, semifinished products or intermediate products, such as, for example, granules or powders, which must pass through another shaping process, such as, for example, melting, casting or extrusion.

Brief Description of the Drawing

Figure 1 is a schematic cross-section of a surface superstructure having protuberances according to the invention.

Detailed Description of the Preferred Embodiments

The structured surfaces of the articles according to the invention have particularly large contact angles. This substantially prevents the wetting of the surface and leads to rapid drop formation of water. With an appropriate inclination of the surface, the drops of water can roll off the protuberances, picking up dirt particles and thus simultaneously cleaning the surface.

Surfaces for the purpose of the present invention may not only be hydrophobic but may also be oleophobic. This property extends the ranges of use of the structured surfaces also to include areas where oil-containing liquids or dirt are to be expected, for example road, rail and air traffic, and in industrial production plants.

Articles having surfaces structured according to the invention can be very easily cleaned. Where rolling-off drops of, for example, rainwater, dew or other water occurring in the field of use of the article are not sufficient for cleaning, the articles can be cleaned by simply washing off with water.

For adhesion to a surface or for multiplication on a surface, bacteria and other microorganisms require water, which is not available on the hydrophobic surfaces of the

present invention. Surfaces structured according to the invention inhibit or prevent the growth of bacteria and other microorganisms and are thus bacteriophobic and/or antimicrobial.

The characterization of surfaces with regard to their wettability can be effected by measuring the surface energy. This quantity is obtainable, for example, through the measurement of the contact angle of various liquids on the smooth material (K.D. Owens, R.C. Wendt, J. Appl. Polym. Sci. 13, 1741 (1969)) and is stated in mN/m (milli-Newton per meter). Determined according to Owens et al., smooth polytetrafluoroethylene surfaces have surface energy of 19.1 mN/m, the contact angle with water being 110°. In general, hydrophobic materials have a contact angle of over 90° with water.

The contact angle or the surface energy is expediently determined on smooth surfaces in order to ensure better comparability. The material property "hydrophobicity" is determined by the chemical composition of the uppermost molecular layer of the surface. A large contact angle or lower surface energy of a material can therefore also be achieved by coating methods.

Surfaces according to the invention have larger contact angles than the corresponding smooth materials. The macroscopically observed contact angle is thus a surface property which reflects the material properties plus surface structure.

A particularly low surface energy is necessary when not only hydrophobic but also oleophobic behaviour is required. This is the case in particular with nonsolid, oily dirt. This in fact leads, in the case of nonoleophobic surfaces, to wetting with oil, which has a permanent adverse effect on the stated properties. For such applications, the surface energy of the smooth, unstructured surfaces should be below 20 mN/m, preferably 10 to 20 mN/m.

The surface properties of the surfaces according to the invention are dependent on the height, the shape and the spacing of the protuberances or protrusions. Protuberances having an average height of 50 nm to 10 μm and an average spacing of 50 nm to 10 μm have proven useful.

For specific fields of use or materials to which the articles are applied, other dimensions of the structure according to the invention may also be used.

The average height of the protuberances is therefore preferably 50 nm to 4 μm with an average spacing of 50 nm to 10 μm. Alternatively, the average height of the protuberances may be 50 nm to 10 μm with an average spacing of 50 nm to 4 μm. Particularly preferably, the protuberances have a height of 50 nm to 4 μm with an average spacing of 50 nm to 4 μm.

The ratio of height to width of the protuberances, the aspect ratio, is likewise important. The protuberances preferably have an aspect ratio of from 0.5 to 20, more preferably from 1 to 10, and particularly preferably from 1 to 3.0.

In addition to the structural properties of the material the chemical properties thereof are also important for achieving the required small contact angles. Here, the chemical composition of the uppermost monolayer of the material is particularly decisive.

Surfaces according to the invention can therefor be produced from materials which already exhibit hydrophobic behavior before the structuring of their surface. These materials contain a particular bulk polymers with polytetrafluoroethylene, polyvinylidene fluoride or polymers of perfluoroalkoxy compounds, either as homo- or copolymers or as a component of a polymer blend.

Also possible are mixtures of polymers with additives, which align in the shaping process in such a way that hydrophobic groups predominate on the surface. Suitable additives are fluorinated waxes, for example the Hostaflons* from Hoechst AG.

The structuring of the surface can be carried out after the hydrophobic coating of a material.

The chemical modifications can also be carried out after shaping so that the protuberances can be subsequently provided with a material having a surface energy of 10 to 20 mN/m.

Since the chemical properties of the uppermost monopolymer of the material are particularly important with respect to the contact angle, surface modification with compounds which contain hydrophobic groups may be sufficient

to achieve the desired surface properties.

Processes of this type include covalent bonding of monomers or oligomers to the surface by a chemical reaction, for example treatments with alkylfluorosilanes, such as Dynasilan* F 8261 from Sivento Chemie Rhienfelden GmbH, or with fluorinated ormoceren.

Processes in which radical sites on the surface are initially produced and are reacted, in the presence or absence of oxygen, with monomers capable of radical polymerization may furthermore be mentioned. The activation of the surface can be effected by means of plasma, UV, or radiation and special photoinitiators. After the activation of the surface, i.e. production of free radicals, the monomers may be polymerized onto the surface. Such a process generates a mechanically resistant coating.

The coating of material or a structured surface by plasma polymerization of fluoroalkenes or perfluorinated or partially fluorinated vinyl compounds has proven particularly useful.

The imparting of hydrophobic properties to a structure surface by means of an HF hollow cathode plasma source with argon as carrier gas and C_4F_8 as monomer at a pressure of about 0.2 mbar is a technically simple and elegant variant for subsequent coating.

In addition, an already produced article can be coated with a thin layer of a hydrophobic polymer. This can

* Trade-mark

be effected in the form of a finish or by polymerization of corresponding monomers on the surface of the article. Solutions or dispersions of polymers, such as, for example, polyvinylidene fluoride (PVDF), or reactive finishes can be used as the polymeric finish.

Suitable monomers for polymerization on the materials or their structured surfaces are in particular alkylfluorosilanes, such as Dynasilan* F 8261 (Sivento Chemie Rheinfelden GmbH, Rheinfelden).

The shaping or structuring of the surfaces can be effected by impression/rolling or simultaneously during macroscopic shaping of the article, such as, for example, casting, injection molding or other shaping methods. Corresponding negative shapes of the desired structure are required for this purpose.

Negative shapes can be produced industrially, for example by means of the Liga technique (R. Wechsung in Mikroelektronik, 9, (1995), page 34 et seq.). Here one or more masks are first produced by electron beam lithography according to the dimensions of the desired protuberances. These masks serve for exposure of a photoresist layer by deep X-ray lithography, with the result that a positive shape is obtained. The intermediate spaces in the photoresists are then filled by electrodeposition of a metal. The metal structure thus obtained is a negative shape for the desired structure.

* Trade-mark

In another embodiment of the present invention, the protuberances are arranged on a somewhat coarser superstructure (Fig.1).

The protuberances have the above-mentioned dimensions and can be applied to a superstructure having an average height of 10 μm to 1 mm and an average spacing of 10 μm to 1 mm.

The protuberances and the superstructure can be formed by mechanical impression simultaneously or in succession, applied by lithographic methods or by shaping.

Such "double" structuring has proven useful particularly in the case of course dirt and has a higher mechanical load capacity compared with the "single" microstructuring.

The protuberances and the superstructure may have a periodic arrangement. However, stochastic distributions of the dimensions of the superstructure and of the protuberances are also permissible, simultaneously or independently of one another.

In the case of surfaces having a superstructure, as in the case of surfaces only having a microstructure, the shaping or structure of the surfaces is expediently effected in one operation. Subsequent imparting of hydrophobic properties or chemical modification of an already produced "doubly" structured surface is of course also possible.

Surfaces produced according to the invention are transparent from structuring smaller than 400 nm and are

therefore suitable for all applications in which high transmittance or good optical properties are important. In particular, the production or coating of headlamps, windscreens, advertising surfaces or coverings of solar cells (photovoltaic and thermal) may be mentioned here.

A further field of use of the surfaces according to the invention is in containers to be emptied without leaving a residue or holders to be rapidly cleaned, such as, for example wafer holders in semiconductor production. Within their production process, wafers are transported with special holders (cassettes) into various baths. To avoid transfer of the various bath liquids, cleaning steps, in particular for the holders, are required. The cleaning or drying steps are dispensed with if the respective bath liquid drips off completely from the holder on removal of the wafer from the bath.

Surfaces according to the invention are therefore extremely suitable for the manufacture of products whose surface promotes the running off of liquids. Surfaces according to the invention are preferably used for manufacturing objects which are self-cleaning as a result of water running off. Preferred products are containers, transparent bodies or holders.

The example below is intended to describe the present invention in more detail without restricting its scope.

Example

A negative shape was produced by UV lithography of a photosensitive plastic and subsequent electroforming with nickel. This shape was used to cast a polycarbonate film having a microstructure with protuberances of about 2 μm wide (measured at half height) and about 4 μm high with a spacing of 4 μm. These protuberances are arranged on a superstructure having a height of about 23 μm and a spacing of about 48 μm. The structure of the shape has the same dimensions with opposite sign. Fig. 1 shows a schematic cross-section (abscissa and ordinate in [μm]).

The polycarbonate film structured in this manner was then rendered hydrophobic with Dynasilan* F 8261 (Sivento Chemie Rheinfelden GmbH, Rheinfelden).

A film rendered hydrophobic in the same manner but unstructured had a contact angle with water of 109.8 + 0.4° and a surface energy of less than 20 mN/m (determined according to Owens et al.) and the structured film a contact angle of 150°. Even stubborn contamination with oily substances could be removed by simply washing off with water.

*Trade-mark

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An article having a structured surface, wherein the structured surface has protuberances having an average height of 50 nm to 10 μm and an average spacing of 50 nm to 10 μm and the structured surface is made of a material which is hydrophobic to such an extent that the material has, when unstructured, a surface energy of 10 to 20 mN/m.

2. The article according to claim 1, wherein the protuberances have an average height of 50 nm to 4 μm.

3. The article according to claim 1, wherein the average spacing of the protuberances is 50 nm to 4 μm.

4. The article according to claim 1, wherein the protuberances have an average height of 50 nm to 4 μm and an average spacing of 50 nm to 4 μm.

5. The article according to any one of claims 1 to 4, wherein, the protuberances have an aspect ratio of from 0.5 to 20.

6. The article according to claim 5, wherein the protuberances have an aspect ratio of from 1 to 10.

7. The article according to claim 5, wherein the protuberances have an aspect ratio of from 1 to 3.0.

8. The article according to any one of claims 1 to 7, wherein the protuberances are applied to a superstructure having an average height of 10 μm to 1 mm and an average spacing of 10 μm to 1 mm.

9. The article according to any one of claims 1 to 8, wherein the material of which the surface is made is

(i) polytetrafluoroethylene, polyvinylidene fluoride or a polymer of a perfluoroalkoxy compound,

(ii) a mixture of a polymer and a fluorinated wax.

(iii) a coating made by a treatment with an alkylfluorosilane or fluorinated ormoceren, or

(iv) a coating made by radical polymerization of a fluoroalkene or a perfluorinated or partially fluorinated vinyl compound.

10. The article according to any one of claims 1 to 8, wherein the material of which the surface is made is a coating made by a treatment with an alkylfluorosilane.

11. The article according to claim 8, wherein the protuberances have an average height of 4 μm and an average spacing of 4 μm, and the superstructure has an average height of about 23 μm and an average spacing of about 48 μm.

12. A process for producing the article as defined in any one of claims 1 to 8, which comprises:

forming the protuberances by mechanical impression or lithographic etching on a surface of the article, or simultaneously with macroscopic shaping of the article, wherein the surface is made of the material having, when unstructured, a surface energy of 10 to 20 mN/m.

13. A process according to claim 12, wherein the material of which the surface is made is

(i) polytetrafluoroethylene, polyvinylidene fluoride or a polymer of a perfluoroalkoxy compound,

(ii) a mixture of a polymer and a fluorinated wax,

(iii) a coating made by a treatment with an alkylfluorosilane or fluorinated ormoceren or (iv) a coating made by radical polymerization of a fluoroalkene or a perfluorinated or partially fluorinated vinyl compound.

14. A process for producing the article as defined in any one of claims 1 to 8, which comprises:

forming the protuberances by mechanical impression or lithographic etching on a surface of the article or by simultaneously with macroscopic shaping of the article; and

then making the so-structured surface hydrophobic by forming a coating of a material having a surface energy of 10 to 20 mN/m.

15. The process of claim 14, wherein the step of making the structured surface hydrophobic is conducted by a treatment with an alkylfluorosilane or fluorinated ormoceren or by radical polymerization of a fluoroalkene or a perfluorinated or partially fluorinated vinyl compound.

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OTTAWA, CANADA

PATENT AGENTS

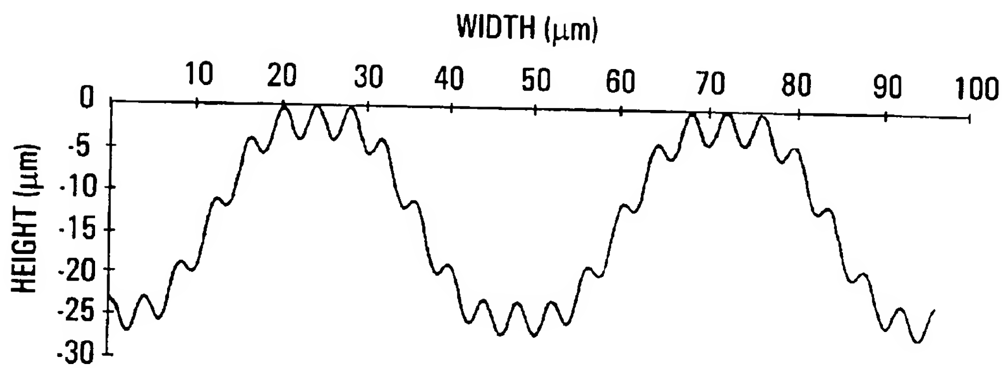

FIG. 1